UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

Note to Reader

Background: As part of its effort to involve the public in the implementation of the Food Quality Protection Act of 1996 (FQPA), which is designed to ensure that the United States continues to have the safest and most abundant food supply. EPA is undertaking an effort to open public dockets on the organophosphate pesticides. These dockets will make available to all interested parties documents that were developed as part of the U.S. Environmental Protection Agency's process for making reregistration eligibility decisions and tolerance reassessments consistent with FQPA. The dockets include preliminary health assessments and, where available, ecological risk assessments conducted by EPA, rebuttals or corrections to the risk assessments submitted by chemical registrants, and the Agency's response to the registrants' submissions.

The analyses contained in this docket are preliminary in nature and represent the information available to EPA at the time they were prepared. Additional information may have been submitted to EPA which has not yet been incorporated into these analyses, and registrants or others may be developing relevant information. It's common and appropriate that new information and analyses will be used to revise and refine the evaluations contained in these dockets to make them more comprehensive and realistic. The Agency cautions against premature conclusions based on these preliminary assessments and against any use of information contained in these documents out of their full context. Throughout this process, If unacceptable risks are identified, EPA will act to reduce or eliminate the risks.

There is a 60 day comment period in which the public and all interested parties are invited to submit comments on the information in this docket. Comments should directly relate to this organophosphate and to the information and issues available in the information docket. Once the comment period closes, EPA will review all comments and revise the risk assessments, as necessary.

These preliminary risk assessments represent an early stage in the process by which EPA is evaluating the regulatory requirements applicable to existing pesticides. Through this opportunity for notice and comment, the Agency hopes to advance the openness and scientific soundness underpinning its decisions. This process is designed to assure that America continues to enjoy the safest and most abundant food supply. Through implementation of EPA's tolerance reassessment program under the Food Quality Protection Act, the food supply will become even safer. Leading health experts recommend that all people eat a wide variety of foods, including at least five servings of fruits and vegetables a day.

Note: This sheet is provided to help the reader understand how refined and developed the pesticide file is as of the date prepared, what if any changes have occurred recently, and what new information, if any, is expected to be included in the analysis before decisions are made. It is not meant to be a summary of all current information regarding the chemical. Rather, the sheet provides some context to better understand the substantive material in the docket (RED chapters, registrant rebuttals, Agency responses to rebuttals, etc.) for this pesticide.

Further, in some cases, differences may be noted between the RED chapters and the Agency's comprehensive reports on the hazard identification information and safety factors for all organophosphates. In these cases, information in the comprehensive reports is the most current and will, barring the submission of more data that the Agency finds useful, be used in the risk assessments.

Jack E. Housenger, Acting Director

Special Review and Reregistration Division

Note to Reader: The reference cited for drinking water concentrations (Birchfield et. Al., 6/10/99, D256746) in the HED risk assessment is incorrect. The reference cited below is the document that was used in the revised preliminary human health risk assessment dated 4-28-00.

Birchfield, N. (USEPA/OPPTS/OPP/EFED) Malathion Drinking Water Concentrations: First Tier Acute and Chronic Exposure Assessments for Surface and Groundwater (3-26-98); [see electronic file: NEEDS TO BE SCANNED]



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON, D.C. 20460

MEMORANDUM

SUBJECT: Malathion Drinking Water Concentrations: First Tier Acute and Chronic

Exposure Assessments for Surface and Groundwater.

Chemical Number: 057701 DB Barcode: D244620

TO: Diana Locke, Risk Assessor

Health Effects Division

Dana Lateulere, Chemical Review Manager **SRRD**

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THRU: Arnet Jones, Chief

Executive Summary:

Based on fate characteristics, model predictions and actual monitoring studies, the Agency predicts malathion will reach drinking water sources from the proposed uses as supported by Cheminova, IR4, and Gowan Co. Surface water concentrations were modeled using the GENEEC model with acute and chronic drinking water levels set with the pesticide use scenarios that produced the highest aqueous pesticide levels. HED has indicated that malathion's degradate, malaoxon is to be included in the tolerance expression for malathion. Thus water concentrations are provided in this document for both malathion and malaoxon.

Table 1. Recommended drinking water concentrations for malathion and malaoxon (Tier I).

compound / exposure type	surface water		ground water	
	estimated concentration (ppb)	source of concentration	estimated concentration (ppb)	source of concentration
malathion / acute	226	GENEEC peak	3.1	Monitoring data
malathion / chronic	21.2	GENEEC 56-day ave.		
malaoxon / acute	96.0	GENEEC peak	3.1	Derived from malathion monitoring data
malaoxon / chronic	75.5	GENEEC 56-day ave.		

EFED recommends that 226 and 96.0 ppb (Table 1) be considered as the highly conservative first tier estimates for acute surface drinking water levels for malathion and malaoxon, respectively. For chronic surface drinking water levels, 21.2 and 75.5 ppb are recommended for malathion and malaoxon, respectively. The chronic malaoxon value exceeds the chronic malathion level because of its longer expected environmental persistence. First tier groundwater concentrations were derived from monitoring data because they were higher than results from the SCIGROW model. The highest detected malathion concentration in groundwater accepted by EFED was 3.1 ppb. Malaoxon was not examined in this study but the same value is expected to be a conservative estimate of malaoxon concentration. EFED recommends exposure estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon in ground water.

This assessment was conducted under guidelines stated in OPP's Interim Approach for Addressing Drinking Water Exposure (November 1997), however, standard modeling techniques were modified to estimate malaoxon concentrations. Malaoxon levels were estimated with the GENEEC model with the <u>assumption</u> that fate variables which were not known are the same as those for malathion. Acceptable environmental fate studies specifically for malaoxon; including degradation, metabolism, mobility, dissipation, and solubility data; would be very useful for future assessments. The numbers provided in this assessment, which are based on predictions of environmental exposure screening models and a preliminary assessment of field monitoring data, are intended to provide IED with conservative first-tier estimates for their human exposure calculations. If the estimated concentrations in this memo cause HED's calculations to exceed human health levels of concern, then refinement of this assessment will be required.

Environmental Fate

Based on all the data submitted, EFED concludes that the primary route of dissipation of malathion in surface soils appears to be aerobic soil metabolism. Supplemental data submitted by the registrant shows malathion degrades in soils with a half-life $(t_{1/2})$ of ≤ 1 day on Blackoar loam soil (pH 6.1). For modeling this half-life value was multiplied by a factor of three to estimate a 90th percentile $t_{1/2}$ value, thus a 3-day half-life was used. This half-life is the same as the value used by USDA in malathion modeling (USDA 1991). EFED notes that longer half-

lives (6.9 days) have been reported on sand (CalEPA 1996). Laboratory half-lives for anaerobic aquatic metabolism (<2.5 days) and hydrolysis (6.21 days at pH 7, 12 hours at pH9) indicate that these are also important routes of dissipation. Conversely, the compound is moderately stable to aqueous ($t_{1/2} = 71$ and 98 days) and soil photolysis ($t_{1/2} = 173$ days) and does not volatilize appreciably ($\le 5.1\%$ volatilized after 16 days).

Data presented to the Agency demonstrate that malathion is extremely mobile and thus runoff and leaching may be major routes of dissipation. Acceptable leaching data on parent malathion indicate that it is mobile in all soils tested [$K_ds = 0.82-2.47$ L/kg, $K_{oc}s = 151-308$ L/kg]. Terrestrial and aquatic field dissipation data indicate rapid dissipation ($t_{1/2} = <2$ days). Malathion has been detected in ground water in three states at levels ranging from 0.007 to 6.17 ppb (USEPA 1992). Based on these data, EFED concludes that malathion has the potential to contaminate surface and ground water.

Malathion mono- and dicarboxylic acids, malaoxon, ethyl hydrogen fumarate, diethyl thiosuccinate, and CO₂ are degradates that have been found in malathion laboratory and field studies. Time course studies on malaoxon production on sand and soil have been published (CalEPA 1993) showing levels to increase over time. Maximal measured malaoxon concentration relative to initial malathion concentrations were 1.4% (after ~10 days on sand) and 10.7% (after 21 days on soil). Measurements past 21 days were not made. In the aerobic soil metabolism study submitted by the registrant 1.8% conversion to malaoxon was the maximum level observed on the Blackoar loam soil, thus 10.7% conversion appears to be a conservative conversion value.

EFED does not have a complete environmental fate database for malaoxon but based on its chemical similarity to malathion (sulfur is replaced by oxygen); the parent and its degradate are expected to have similar chemical properties. However, the biological properties of malaoxon are notably different in that it is more toxic than malathion. The aerobic half-life of malaoxon has been reported as 3 and 7 days in basic and acidic soils, respectively (Paschal and Neville 1976). This longer half-life is proposed to be a result of malaoxon's biocidal effect on soil microbes which contribute to malathion's degradation.

SURFACE WATER ASSESSMENT:

EFED uses the GENEEC screening model to estimate surface water concentrations for first-tier exposure assessments. GENEEC (USEPA 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple and require data which is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to

1 and 5% of the applied rate for ground and aerial spray application, respectively.

Standard GENEEC modeling is inappropriate for malaoxon concentrations because the model assumes initial concentrations are highest which is not the case with malaoxon which increases over a period of weeks. In this case EFED chose a conservative scenario for modeling malaoxon concentrations by assuming that 10.7% of each malathion application is converted to malaoxon, thus for the purposes of GENEEC malaoxon was applied at 10.7% the rate of malathion. Data used for modeling were not ideal. The physical parameters used for malaoxon were those of malathion based on their chemical similarity. For the purpose of modeling EFED has attempted to estimate the upper 90th percentile of malaoxon's aerobic soil half-life value by multiplying 7 days (Paschal and Neville 1976) by a factor of three resulting in the model input value of 21 days. The aqueous half-life used was 107 days (based on malathion hydrolysis at pH 5), respectively. Both half-lives are expected to be conservative. The hydrolysis data for malathion is expected to be similar to malaoxon and is used in the absence of a half-life value in water with microbial activity.

Modeling results indicate that malathion has the potential to move into surface waters. Based on the inputs shown in Table 2 the peak GENEEC estimated environmental concentrations (EEC) of malathion and malaoxon in surface water is 226 and 96.0 ppb, respectively (Table 3). This estimate is based on the maximum application rate for citrus which represents the highest application rate for any crop used to support residue tolerances. EFED notes that higher use rates are reported on product labels but the registrant has stated they will not support rates greater than those defined in crop residue studies.

Acute exposure

EFED recommends that 226 and 96.0 ppb be adopted as a highly conservative estimates of acute drinking-water exposure for malathion and malaoxon, respectively, based on the peak GENEEC value obtained with use on citrus and cotton.

Chronic exposure

EFED recommends that 21.2 and 75.5 ppb be adopted as a highly conservative estimate of chronic drinking-water exposure for malathion and malaoxon, respectively, based on concentrations for the 56 day average GENEEC value obtained with use on citrus and cotton.

Table 2. GENEEC Environmental Fate Input Parameters (values are for malathion unless otherwise stated.)

DATA INPUT	INPUT VALUE	DATA ASSESSMENT	SOURCE
Application Rate	0.18-6.25 lbs ai/A		•
Maximum Number of Applications	1-25		•
Application Interval	3-30 days		·
Batch Equilibrium (Koc)	151 ml/g	Acceptable	MRID 41345201
Aerobic Soil Metabolism	malathion: $t_{1/2} = 3$ day malaoxon: $t_{1/2} = 3-7$ day (model input = 21 days)	Supplemental Supplemental	MRID 41721701 Paschal and Neville 1976
Solubility	145 ppm	Acceptable	Reported by registrant
Aerobic Aquatic Metabolism	t _{1/2} = 3.3 day`	Acceptable	MRID 42271601, 43163301
Hydrolysis (used for malaoxon aerobic aquatic t ₁₇)	t ₁₇ = 104 day	Acceptable	MRID 40941201
Photolysis	t _{1/1} = 94 days	Acceptable	MRID 41673001, 43166301

use-rates and the use scenario for cotton were analyzed by GENEEC modeling.

GENEEC EEC $(\mu g/L)$ application rate crop / interval (lbs ai / malathion malaoxon (days) A) method 56-day ave peak max# peak 56-day ave annually 0.18 Orange/7 aerial 10 8.24 0.78 3.10 2.44 grapefruit/7 Jemon/7 lime/7 tangerine/7 tangelo/7 kumquat/7 0.50 Flax 1 11.4 ground 1.07 1.82 1,43 Cotton/3 25 181 16.9 96.0 75.5 ground 5.0 Pineapple/7 3 ground 224 20.9 47.3 37.2 5.0 Chestnut/7 4 225 57.1 ground 21.1 44.9 6.25 Orange/30 ground 226 21.2 37.1 29.2 grapefruit/30 lemon/30 lime/30 tangerine/30

EFED notes that there is limited information available on the conversion of malathion to malaoxon during drinking water treatment. In a limited sampling of water entering and leaving a water treatment plant both malathion and malaoxon levels generally decreased after treatment, however, one sample showed an increase in malaoxon (USDA 1997). EFED recognizes that conversion of malathion to malaoxon may be more efficient during water treatment than under conditions in the field, thus malaoxon may be present at a higher concentration relative to malathion after water processing.

GROUND WATER ASSESSMENT:

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As EFED noted above, malathion has some mobility characteristics similar to other chemicals that have been detected in ground water. In addition, malathion has been detected in ground water in at levels ranging from 0.03 to 6.17 ppb in California (1 detection out of 499 wells sampled at a concentration of 0.32 ppb), Mississippi (2 detection out of 263 wells sampled at a range of concentrations of 0.03-0.053 ppb) and Virginia (9 detections out of 138 well sampled at a range of concentration of 0.007-6.17 ppb); as reported in the EPA/OPP/EFED/EFGWB EPA Pesticides in Ground Water Data Base 1971-1991, National Summary. ERB1/EFED believes that malathion has the potential for movement into groundwater, especially on soils with low organic matter and high sand content.

Cheminova disputes the ground-water data reported in the PGWDB. In particular, it calls into

question the analytical methods used to generate the data in the Virginia study. In addition, Cheminova indicates that the maximum detection in the study was 3.12 ppb, not 6.17 ppb. Noting Cheminova's doubts for the Virginia data, EFED suggests a ground-water concentration estimate of 3.1 ppb for malathion. This value is more conservative than SCI-GROW modelling results using use parameters for citrus or cotton as stated above. Since this monitoring result is specific for malathion EFED assumes the concentration of malaoxon cannot exceed the concentration of malathion. Thus, EFED suggests conservative ground water concentration estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon.

MONITORING DATA

EFED is presently reviewing a number of malathion field monitoring studies. This data may add additional insight into malathion behavior in relation to surface and ground waters. A preliminary interpretation of the data suggests that GENEEC modeling results used here are conservative in assessing exposure to malathion through drinking water. As additional information is reviewed its effect on the conclusions reached in this memo will be evaluated and included in refined tier 2 water assessments if required.

REFERENCES

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